APPLICATION OF THE CURRENT-IMPULSE RELAXATION TECHNIQUE TO THE MERCURY (I) SYSTEM

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ABSTRACT

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Because kinetic results of investigations of the electrochemical reduction of mercury(I) by many different methods were very inconsistent this process was re-investigated using the current-impulse relaxation technique.

In the current-impulse technique an electrochemical system is displaced from equilibrium by a constant current impulse of brief time duration. The double layer is linearly charged to overpotentials of not more than a few millivolts. The differential capacitance can be calculated from the slope of the charging curve and the applied current. The charge from the impulse is consumed by the electrochemical reaction and charge-transfer kinetic parameters can be determined from the overpotential-time curves.

Using this technique, the electrochemical reduction of mercury(I) at a hanging mercury drop electrode in 1.0 $\underline{M}$ perchloric acid at 25^0 C was investigated at concentrations from 5×10^{-6} to 1×10^{-2} $\underline{M}$ mercurous perchlorate. The differential capacitance was observed to rise sharply over the range of potentials corresponding to these concentrations. The kinetic parameters deduced from the relaxation measurements were higher than the results of previous investigations because of the absence of mass-transport control at short times.

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TABLE OF CONTENTS

Page

I. INTRODUCTION 1

- A. Brief Explanation of Current-impulse Technique 1
- B. Chemistry of Hg(I) 4
- C. Previous Studies of Kinetics for Reduction of Hg(I) and Results 10
- D. Summary of Results of This Study Compared to Previous Studies 29

II. EXPERIMENTAL 32

- A. Reagents 32
- B. Solutions 33
- C. Cell and Electrodes 33
- D. Instrumentation 34

III. RESULTS 38

- A. Capillary Data 38
- B. Capacitance Data 39
  1. Variance with current for charging capacitance 39
  2. Comparison of charging and relaxation values of capacitance 42
  3. Capacitances compared to those of Weir and Sluyters-Rehbach and Sluyters . . 42
  4. Current density calculated from capacitance and change with concentration of Hg_2^{2+} to determine α 45
  5. Comparison of values of i_a^o and α with those of previous investigations . . 52

IV. CONCLUSION 54

BIBLIOGRAPHY 55

LIST OF TABLES

Table Page

1. Comparison of the present kinetic results with the results of previous studies 31

2. Drop period, drop mass, and spherical drop area in solutions of varying concentration of $Hg_2(ClO_4)_2$ in 1.00 $\underline{M}$ $HClO_4$ 38

3. Differential capacitance data from charging and from relaxation experiments for 5.12×10^{-6}, 1.026×10^{-3}, 1.026×10^{-2} $\underline{M}$ $Hg_2(ClO_4)_2$ in 1.00 $\underline{M}$ $HClO_4$, pulse duration 200 nsec 41

4. Zero-current capacitance from charging and from relaxation data for 5×10^{-6} to 1×10^{-2} $\underline{M}$ $Hg_2(ClO_4)_2$ in 1.00 $\underline{M}$ $HClO_4$ 43

5. Values of apparent exchange current density for 5×10^{-6} to 1×10^{-2} $\underline{M}$ $Hg_2(ClO_4)_2$ in 1.00 $\underline{M}$ $HClO_4$ 49

6. Corrected values of apparent exchange current density for 5×10^{-6} to 5×10^{-5} $\underline{M}$ $Hg_2(ClO_4)_2$ in 1.00 $\underline{M}$ $HClO_4$ 52

LIST OF FIGURES

Figure	Page
1. Potentiostatic arrangement for Gerisher and Staubach's potentiostatic measurements . .	13
2. Arrangement for Gerisher and Krause's double-pulse galvanostatic measurements .	15
3. Circuit for Weir's adsorption model	28
4. Electrode system for the present investigation	34
5. Schematic representation of interconnection of cell and instruments in the present investigation	37
6. Differential capacitance from charging and relaxation procedures	40
7. Differential capacitance as a function of potential	44
8. Typical charging curves	46
9. Typical relaxation and log η vs t curves . .	47
10. Reaction order plot in 1.0 M $HClO_4$ at 25^0 C.	50

I. INTRODUCTION

A. Brief Explanation of Current-impulse Relaxation Technique

The current-impulse relaxation technique is a relatively new method of studying the kinetics of fast electrode reactions. It is a variant of the charge step method proposed simultaneously by Delahay (6,7) and Reinmuth (24,25). The principle is as follows: The electrode being studied is initially at equilibrium. The charge density on the electrode is changed abruptly by applying a constant current impulse of brief duration in such a way that the electrochemical cell is essentially at open circuit once charging is completed. The potential departs from the equilibrium value as a result of the change of charge density. The increment of charge applied to the electrode is consumed progressively by the electrode reaction, and the potential drifts back to its initial equilibrium value. The overvoltage-time variations depend on the coulombic content of the impulse, the double layer capacitance, and the characteristic electrode process. By restriction of the coulombic content of the impulse and reduction of the time interval before relaxation data are acquired the kinetic parameters of the charge-transfer process are found without correction for mass-transport contributions. Study of electrode kinetics from overvoltage-time curves is therefore possible.

The increment of charge is:

$$\Delta q = q_o - q_i \qquad (1)$$

where q_i is the charge density at the equilibrium potential for the electrode reaction $O + ne^- = R$ and q_o is the charge density immediately after charging. It is assumed that the charging time is so short that leakage by the charge transfer reaction can be neglected during charging. The overvoltage η ($\eta = E - E_e$, where E_e is the equilibrium potential) at time t after charging is:

$$\eta = (q - q_i)/C_d \qquad (2)$$

where q is the charge density at time t and C_d is the differential capacitance of the electrode. It is usually assumed that variations of E are so small ($|\eta_o| < 5$ mv. approximately) that C_d is constant. The signs in Eqn. 2 are consistent with the definition $\eta = E - E_e$ and the dependence of q on E, namely, $\eta \gtrless 0$ for $q - q_i \gtrless 0$. The charge density q is:

$$q = q_o + \int_o^t i\, dt \qquad (3)$$

where i is the faradaic current density for discharge of the double layer and the integral is equal to the quantity of electricity used by the electrode at time t. The integral is preceded with a plus sign, i.e. $q \gtrless q_o$ for $i \gtrless 0$, in agreement with the convention of regarding a net cathodic current as positive and a net anodic current as negative. It follows from Eqns. 1 to 3 that

$$\eta = [(q_o - q_i)/C_d] + (1/C_d) \int_o^t i\, dt \qquad (4)$$

$$= \eta_{t=0} + (1/C_d) \int_o^t i\, dt$$

where

$$\eta_{t=0} = \Delta q/C_d \qquad (5)$$

is the overvoltage after charging at $t = 0$.

The derivation of the solution of Eqn. 4 in which C_d is supposed to be constant requires the explicit form of i as a function of η. The linearized $i - \eta$ characteristic in the absence of mass transfer is:

$$i = i_a^o (nF/\nu_d RT)\eta \qquad (6)$$

where i_a^o is the apparent (i.e., not corrected for the effect of the double layer) exchange current density, ν_d is the stoichiometric number, and F, R, and T are as usual. Note that $i \gtrless 0$ for $\eta \gtrless 0$ and that Eqn. 6 holds well for $|\eta| \lesssim 5$ mv., approximately. The combination of Eqns. 4 and 6, and the solution of the resulting equation yield the equation

$$\eta/\eta_{t=0} = \exp[-(i_a^o/C_d)(nF/\nu_d RT)t] \qquad (7)$$

which is identical to the relationship for the voltage-time variations for discharge of a capacitor across a constant resistance. The overvoltage decays exponentially with time, and a plot of log $|\eta|$ against t is linear. i_a^o is readily computed from the slope of the plot if n/ν_d and C_d (per cm^2) are known, and the transfer coefficient is deduced from the variations of i_a^o with the concentrations of O and/or R. The differential capacitance C_d which is needed in the computation of i_a^o is obtained from the slope of the charging curve and the measured current or may be determined from Eqn. 5 with q_o known and η_o determined by extrapolation of the log $|\eta|$ versus t plot to $t = 0$.

B. Chemistry of Hg(I)

The chemistry of Hg(I) is complicated by two factors: (1) the fact that it is a dimer and (2) its disproportionation. Both of these factors have long been realized.

There have been many lines of evidence showing the binuclear nature of Hg_2^{2+}. A few of these may be noted:

(1) Mercurous compounds are diamagnetic both as solids and in solution, whereas Hg^+ would have an unpaired electron.

(2) X-ray determination of the structures of several mercurous salts shows the existence of individual Hg_2^{2+} ions.

(3) The Raman spectrum of an aqueous solution of mercurous nitrate contains a strong line which can only be attributed to an Hg - Hg stretching vibration (39).

These and other historical evidence are discussed by Sidgwick (31).

The dissociation of the Hg_2^{2+} dimer has been postulated to occur in solution chemistry of the mercurous ion.

Higginson (15) on studying the ultra-violet absorption of mercurous perchlorate in dilute (10^{-2} - 10^{-3} $\underline{M}$) perchloric acid solutions observed deviations from Beer's law below 10^{-6} $\underline{M}$ mercurous perchlorate and suggested this was because of a significant degree of dissociation of the dimer at these concentrations. This led to a value of $K_{diss} = [Hg^{+}]^2/[Hg_2^{2+}] = 1.6 \times 10^{-7}$ and limits of $10^{-8} - 10^{-6}$. Interference from perchloric acid was not detectable.

Cartledge (5) also postulated the existence of Hg^{+} as a chain carrier in Eder's reaction. He calculated a normal potential of the half reaction $Hg(\ell) \rightleftharpoons Hg^{+}(aq) + e^{-}$ as -1.71 volts. Combining this potential with other mercury potentials he showed that the dissociation of the ordinary mercurous ion Hg_2^{2+} in solution is attended by a standard free energy change of 42 Kcal., from this $pK_d = 31$ can be derived, which is much larger than that of Higginson.

Kolthoff and Barnum (17) in studying the anodic waves of cysteine at the dropping mercury electrode postulated the existence of a species HgSR, the anodic reaction given by the equation $RSH + Hg = HgSR + H^{+} + e^{-}$. They postulated that at mercurous concentrations of the order of 10^{-20} $\underline{M}$ practically all of the mercurous is present in solution as Hg^{+} and not as Hg_2^{2+}. From their data a $pK_d = 18$ can be estimated.

In 1957 Moser and Voigt (22) using ^{203}Hg and determining the ratio of this in an aqueous phase and an equilibrated organic phase calculated a dissociation constant $K_d = 10^{-7}$ for the reaction $Hg_2^{2+} = 2Hg^{+}$.

The Hg^{+} ion has also been postulated as a reaction intermediate in the reaction of mercury(I) with cerium(IV) studied by McCurdy and Guilbault (21). Using 2.5 - 0.28 mM Ce^{4+} and 1.82 - 0.161 mM Hg_2^{2+} in 2.0 M perchloric acid at 50^{0} C they found the reaction rate to be directly proportional to the Hg_2^{2+} and Ce^{4+} concentrations but not to be affected when Hg^{2+} was added. They postulated the following mechanism:

$$Ce^{4+} + (Hg\text{-}Hg)^{2+} \xrightarrow[\text{slow}]{k_1} Ce^{3+} + Hg^{1+} + Hg^{2+}$$

$$Ce^{4+} + Hg^{1+} \xrightarrow[\text{fast}]{k_2} Ce^{3+} + Hg^{2+}$$

where the rate determining step is the breaking of the $(Hg\text{-}Hg)^{2+}$ bond, concomitant with transfer of an electron.

On studying the reaction of Co(III) with Hg_2^{2+} in aqueous perchloric acid Rosseinsky and Higginson (27) also postulated the Hg^{+} ion as an intermediate though also stating the possibility of Hg_2^{3+}. The concentration of ClO_4^{-} ion was found not to affect this reaction. They postulated the following mechanism:

$$Co^{3+} + Hg_2^{2+} \longrightarrow Co^{2+} + Hg^{2+} + Hg^{1+}\ (\text{or } Hg_2^{3+})$$

$$Co^{3+} + Hg^{1+}\ (\text{or } Hg_2^{3+}) \longrightarrow Co^{2+} + (2)\ Hg^{2+}$$

On studying the kinetics of the reaction between Hg_2^{2+} and Tl^{3+} in 3 M $HClO_4$ at 25^{0} C Higginson and coworkers (1) suggested that what Higginson had observed earlier in his ultraviolet studies was not the dissociation of Hg_2^{2+} but the dismutation reaction:

$$Hg_2^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Hg^{2+} + Hg.$$

They postulated the following reaction scheme:

$$Hg_2^{2+} \overset{k_1}{\rightleftharpoons} Hg^{2+} + Hg$$

$$Hg + Tl^{3+} \overset{k_2}{\rightleftharpoons} Hg^{2+} + Tl^{1+} \quad .$$

In this reaction they found a dependence on the concentration of ClO_4^- and explained it by the complexation of Hg_2^{2+} and ClO_4^-. They determined $K_a = 1.0$ 1-mole^{-1} for $Hg_2^{2+} + ClO_4^- \rightleftharpoons Hg_2ClO_4^+$.

Moser and Voigt (23) undertook the study of this dismutation reaction using highly dilute mercurous nitrate solutions. Radioactive tracer techniques were used to permit measurements in the 10^{-7} N range. The free mercury was extracted into non-polar organic solvents to measure the extent of dismutation. The equilibrium constant for the dismutation reaction was found to be 5.6×10^{-9}. The solubility of mercury in aqueous solutions was found to be $(3.0 \pm 0.1) \times 10^{-7}$ M at 25° C.

Hietanen and Sillen (14) used emf methods to measure the equilibrium constants for the reaction: $Hg^{2+} + Hg(\ell) = Hg_2^{2+}$ at an H^+ concentration of 0.01 M in various nitrate and perchlorate solutions. The equilibrium constant at infinite dilution was calculated to be 88 ± 3 at 25° C which agrees well with Schwarzenbach and Anderegg's value of $K = 84.8 \pm 2$ (29). The equilibrium constant varied little with nitrate concentration but increased strongly with perchlorate ion concentration. They calculated $K_a = 0.9$ liter mole^{-1} for the reaction

$$Hg_2^{2+} + ClO_4^- = Hg_2ClO_4^+$$

which agrees well with that determined by Higginson.

Wolfgang and Dodson (38) have suggested that the very rapid isotopic electron exchange between Hg^{2+} and Hg_2^{2+} i.e.

$$Hg_2^{2+} + Hg^{*2+} \longrightarrow Hg_2^{*2+} + Hg^{2+}$$

proceeds through the mechanism

$$Hg_2^{2+} \longrightarrow Hg + Hg^{2+}$$

$$Hg + Hg^{*2+} \longrightarrow Hg_2^{*2+}$$

Their results support the conclusion that the Hg_2^{2+} dismutation is rapidly established.

The dismutation of Hg_2^{2+} has been postulated to contribute to reaction mechanisms.

The homogeneous reduction of mercuric salts in aqueous solutions by molecular hydrogen i.e. $2Hg^{2+} + H_2 \longrightarrow Hg_2^{2+} + 2H^+$ as studied by Korinek and Halpern (18) has been postulated to proceed through the mechanism:

$$Hg^{2+} + H_2 \longrightarrow Hg + 2H^+ \text{ (slow)}$$

$$Hg + Hg^{2+} \longrightarrow Hg_2^{2+} \text{ (fast).}$$

Rosseinsky (26) also postulated the dismutation of Hg_2^{2+} in his study of the reaction between mercury (I) and manganese (III) in aqueous perchlorate. He postulated that the reaction occurred through the following mechanism:

$$Hg_2^{2+} \xrightleftharpoons{k'} Hg^0 + Hg^{2+}$$

$$2Mn^{2+} \xrightleftharpoons{k''} Mn^{4+} + Mn^{2+}$$

$$Mn^{3+} + Hg^0 \xrightarrow{k'} Mn^{2+} + Hg^{1+}$$

$$Mn^{3+} + Hg^{1+} \longrightarrow Mn^{2+} + Hg^{2+} \text{ Rapid}$$

$$Mn^{4+} + Hg_2^{2+} \longrightarrow Mn^{2+} + 2Hg^{2+} .$$

Using the data of Sillen and Hietanen a value of the equilibrium constant for the disproportionation of Hg (I) to Hg (II) and the liquid metal in unimolar perchloric acid can be calculated. For unimolar $HClO_4$ $Hg^{2+} + Hg(\ell) \rightleftharpoons Hg_2^{2+}$ $K = 165 \pm 10$ liter mole^{-1} or K =± 0.0061 mole liter^{-1} for $Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg(\ell)$. From this value and the value for the solubility of mercury a disproportionation constant for $Hg_2^{2+}(aq) \rightleftharpoons Hg^{2+}(aq) + Hg\ (aq)$ in 1.0 M $HClO_4$ of 1.8×10^{-9} mole liter^{-1} can be calculated.

Thus the pertinent equilibria of $Hg_2(ClO_4)_2$ in 1.0 M $HClO_4$ are as follows:

System	Medium	K
$Hg_2^{2+}(aq) = Hg^{2+}(aq) + Hg(\ell)$	Infinite dilution	0.011 M
$Hg_2^{2+}(aq) = Hg^{2+}(aq) + Hg(\ell)$	1.0 M $HClO_4$	0.0061 M
$Hg_2^{2+}(aq) = Hg^{2+}\ (aq) + Hg(aq)$	Infinite dilution	5.5×10^{-9} M
$Hg_2^{2+}(aq) = Hg^{2+}(aq) + Hg(aq)$	1.0 M HClO4	1.8×10^{-9} M
$Hg(\ell) = Hg(aq)$	(independent of ionic strength)	3.0×10^{-7} M
$Hg_2^{2+}(aq) + ClO_4^-(aq) = Hg_2ClO_4^+(aq)$		0.9 M^{-1}

C. Previous Studies of the Kinetics for Reduction of Hg(I) and Results

Since the system Hg(I)/Hg has long been considered a prototype of reversible reactions in electrochemical systems there have been a variety of studies of it by different methods. Since these methods were not all adequate to study the kinetics of such a fast reaction a variety of kinetic parameters has resulted.

In 1948, Rozental and Ershler (28) to determine the applicability of a faradaic impedance method proposed by Ershler (9,10), studied the behavior of a mercury drop electrode in 5×10^{-4} to 1×10^{-2} N solutions of mercurous nitrate in 2.0, 0.2, and 0.02 N perchloric acid. They resolved the cell impedance into series resistive and reactive components. The electrolyte resistance (estimated by conductance measurements in 2 N $HClO_4$) was subtracted from the series resistance. By transforming the resulting series analog of the electrode impedance into its parallel equivalent a correction for the admittance of the double layer was obtained. A value of 40 microfarads cm^{-2} was taken for the differential capacitance at all concentrations in this calculation. Reverse transformation gave series-equivalent values C_R and R_R.

According to the theory of Ershler R_R and $1/\omega C_R$, where ω is the angular frequency, plotted as functions of $\omega^{-1/2}$ should yield straight line plots of identical slope, the intercepts corresponding to $\omega \longrightarrow \infty$ should be zero for the reactive component and a value equal to the charge-transfer resistance for the resistive component. On the plots of Rozental and Ershler the points fall on straight lines, the reactive and resistive plots are however, not parallel but appear to extrapolate to a common zero intercept. The authors conclude that the charge-transfer resistance is thus less than the uncertainty in the measurement of resistance 0.03 ohm cm^2.

The faradaic impedance method was also used by Gerisher and Staubach (13) to determine the kinetics of the Hg(I)/Hg electrode. The authors also carried out a preliminary potentiostatic investigation. To determine the solution resistance in the presence of this highly reversible reaction they found it necessary to extend measurements to quite high frequencies (to 200 kHz). They also realized the necessity of measurement of the differential capacitance. They calculated the series capacitance corrected for trial values of the double layer capacitance, the value which, in accord with theory gave a constant difference between series resistance and reactance independent of frequency, was taken as the correct value, and the difference was the charge-transfer resistance. The impedance was determined in an equal armed bridge by comparison with a resistance and a capacitance in series connection. At the dropping mercury electrode the bridge was balanced so that in the instance of departure of the drop the potential difference was null. Determinations were made in 1, 2, and 4 x 10^{-3} M mercurous perchlorate in 1 M perchloric acid and a plot of log Hg_2^{2+} vs. log i_a^o yields a straight line of slope 0.7 ± 0,2. The k_a^o calculated from this data is 0.00391 cm/sec.

The potentiostatic measurements were observed on an electron beam oscilloscope connected to a potentiostat. Figure (1) shows the principal form of the potentiostatic arrangement. The amplifier had an amplication factor of approximately 2000 and a frequency up to 50 kHz, which because of the large capacitance of the measured object was locally perhaps 10 kHz. The current was measured by an oscilloscope (S) after introduction to a direct current amplifier (V). Since the resistance R_V which served for current measurement had little influence on the potentiostatic arrangement, it was varied without difficulty and adjusted to the actual current flow.

The potentiostat used in these experiments had a time constant of 10^{-5} sec which causes the results to be rather uncertain. The values for the exchange current found by this method were consistently below those found by the faradaic impedance method. This was attributed to the onset of concentration polarization because of the rise time of the potentiostat. The reaction order plot of these data yields a slope of 0.6 ± 0.1.

By comparing the cathodic Tafel slope $(=2.303\nu_d RT/\alpha nF)$ with the slope of the reaction order plot, with the assumption that the rate-determining charge-transfer step is the only

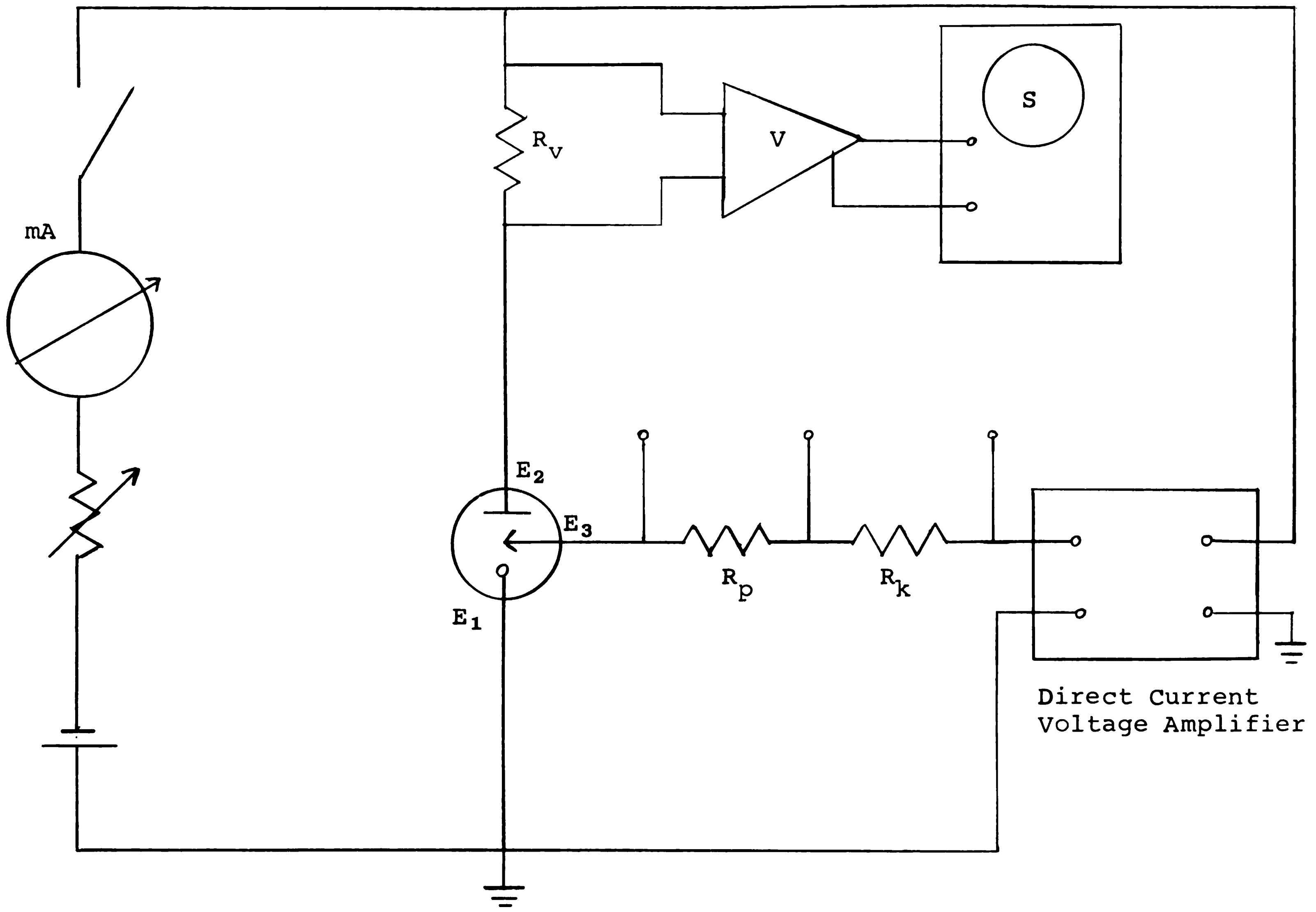


Figure 1. Potentiostatic arrangement for Gerisher and Staubach's potentiostatic measurements.

E_1 = Working electrode, E_2 = Counter electrode, E_3 = Reference Electrode
S = Oscilloscope, V = Amplifier.

charge-transfer step in the overall process, the authors determined $n/\nu_d = 2$ and $1 - \alpha = 0.6 \pm 0.1$. Because $n/\nu_d = 2$ and thus $\nu_d = 1$, they concluded that the mercurous ion traverses the phase boundary undissociated and hence that the charge transfer reaction for electrodeposition is

$$Hg_2^{2+}(aq) + 2\,e^- \longrightarrow 2\,Hg_{metal} + aq.$$

with the assumption of a single charge-transfer step.

In an attempt to resolve the discrepancy between the faradaic impedance and the potentiostatic-step results Gerisher and Krause examined the kinetics of electrodeposition of mercury with the double pulse galvanostatic technique (12).

The current impulse was produced with an electronic generator. The pulse was obtained as follows: A trigger circuit produced a differentiated short needle impulse which was then fed to a monostable multivibrator. At the output of the monostable multivibrator a rectangular impulse was obtained. This was improved in a discriminator, then the long and short pulses were overlapped to obtain the double pulse for the measurement. Impulses from 5μa to 400 mA could be obtained from the pulse generator. The authors state that the slope of the top with long impulses amounted to approximately 2% at 300 μsec, the side steepness of the short impulse depending on the magnitude of the cut off resistance was between 5×10^{-8} and 2×10^{-7} sec.

The arrangement for measurement is given in Figure (2). It consisted essentially of a bridge connection. The

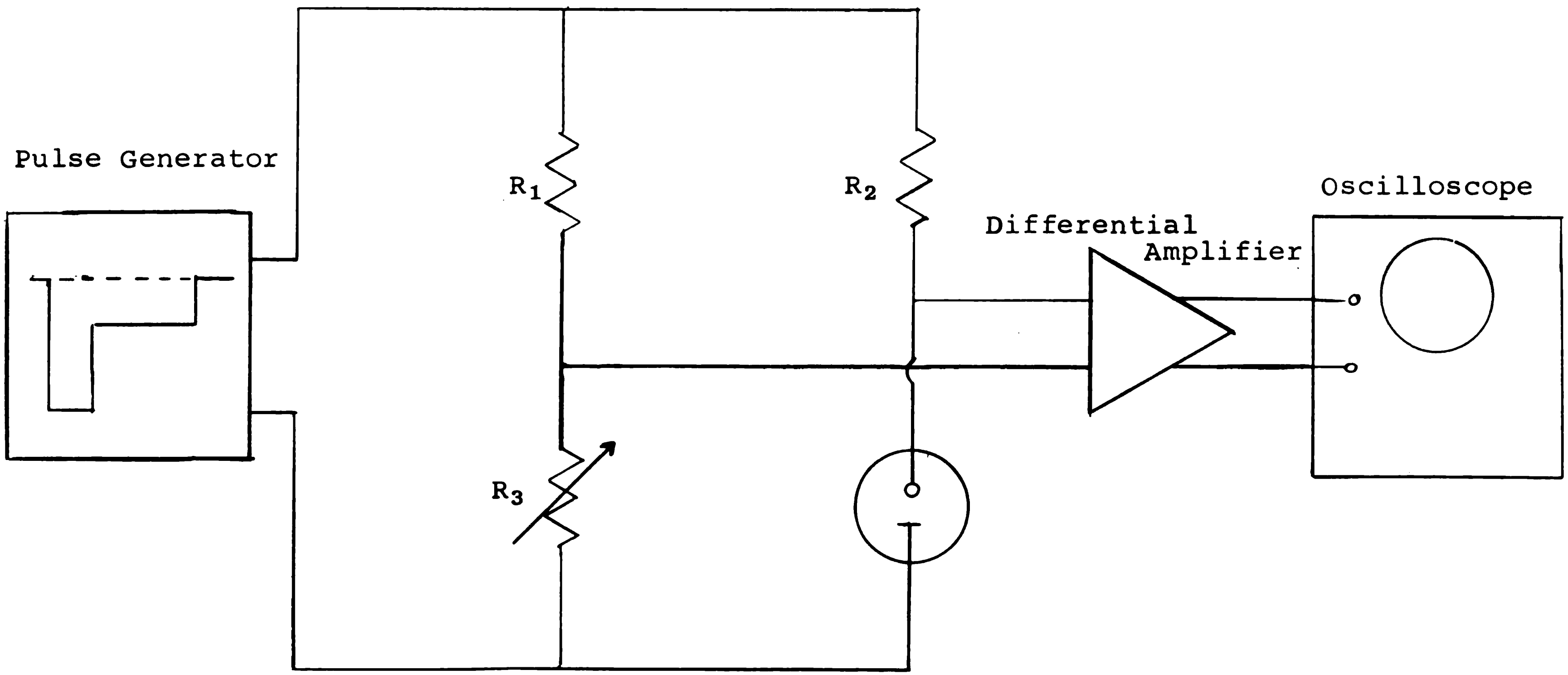


Figure 2. Arrangement for Gerisher and Krause's double-pulse galvanostatic measurements.

electrolyte resistance could be reduced according to its relationship to the magnitude of the transfer resistance of the measurement sensitivity through compensation of the bridge resistance (R_3) situated parallel to the cell. With the correct standard resistance the potential time curve would begin at the null point. The compensating resistance also permitted the measurement of the current. Current and potential measurements were measured with an oscilloscope with a maximum sensitivity of 1 mv/cm. The authors state that equilibrium resulted on the average after 1.5 μsec.

At 25° C, exchange currents were determined for solutions from 5.9×10^{-4} $\underline{M}$ to 3.5×10^{-3} $\underline{M}$ mercurous perchlorate in 1 $\underline{M}$ perchloric acid. These data gave a reaction order plot with a slope of 0.70 ± 0.03 and hence an apparent transfer coefficient of 0.30 ± 0.03 for $n/\nu_d = 2$. The exchange currents were somewhat higher than those reported by Gerisher and Staubach. A $k_a^o = 0.011$ cm/sec can be calculated from these data.

The incongruity of a mechanism involving dissociation of the mercurous dimer prior to charge with the experimentally derived $\nu_d = 1$ was demonstrated by Gerisher and Krause. In addition, they considered the possibility of a disproportionation

$$Hg_2^{2+}(aq) \longrightarrow Hg^{2+}(aq) + Hg(aq).$$

The authors contended that the intermediacy of this reaction would give rise to abrupt concentration polarization for the dissolution process due to insufficient supply of Hg(aq). Because this concentration polarization was not observed for anodic dissolution, even at high current densities, they concluded prior disproportionation is not involved and concluded the mechanism must be that identified by Gerisher and Staubach.

Matsuda, Oka, and Delahay (20) also used the double pulse galvanostatic technique for study of the Hg/Hg(I) system.

The double pulse generator was composed of two single pulse generators which were triggered manually with another pulse generator. The two pulses were mixed in a twin-triode circuit with common cathode. A bridge circuit was used for compensation of the ohmic drop in the cell (2). It was inserted in the cathode circuit of the mixer.

Pulse heights were adjusted by variation of the grid voltages of the mixer with separate battery supplies. Certain precautions were taken to obtain minimum rise and cut off times. The pulse height ratio varied from 2 to 12 in this study. The low residual plate current through the bridge in the absence of pulse generation was compensated with a potentiometer.

The rise and cut off time was approximately 0.2 micro sec for any pulse length. The pulse generators that were used had approximately a 0.2 microsec rise and cut off time and distortion thus resulted from the pulse generators rather than the mixer. The combination of the preamplifiers used in this study, at maximum gain, had a linear response for input voltages up to 80 millivolts. The input voltage did not exceed 50 millivolts in this study (cell resistance of approximately 5.0 ohms). The maximum sensitivity was 0.5 millivolt per centimeter deflection.

Matsuda, Oka, and Delahay, by means of a complete solution of the boundary problem take into account concentration polarization in the galvanostatic technique. They reconsidered the data of Gerisher and Krause and concluded that serious errors in the apparent exchange currents reported by these authors had been introduced by their simplified treatment which assumed concentration polarization to be negligible for preimpulses of one microsecond duration. Delahay and coworkers determined the exchange current densities for solutions from 2.5×10^{-4} to 2×10^{-3} $\underline{M}$ mercurous perchlorate in 0.98 $\underline{M}$ perchloric acid at 25° C. Their corrected exchange current density for 1×10^{-3} $\underline{M}$ mercurous perchlorate is approximately twice the value determined by Gerisher and Krause.

Imai and Delahay (16) in order to illustrate the application of the faradaic rectification technique of Senda, Imai, and Delahay (30) to very rapid charge-transfer reactions made a study of the discharge of mercurous ions.

The general equation for the rectification voltage for control of the mean faradaic current to zero has the following form in the particular case of the discharge of Hg(I) on Hg

$$\frac{\Delta\bar{E}_{\infty}}{V_A^2} = \frac{nF}{RT}\left[\frac{2\alpha - 1}{4} - \frac{\alpha}{2}\,\frac{1 + \mathrm{ctn}\,\theta_a}{1 + \mathrm{ctn}^2\,\theta_a}\right] \qquad (A)$$

where $\Delta\bar{E}_{\infty}$ is the rectification voltage for $t \rightarrow \infty$; V_A the amplitude of the sinusoidal voltage across the faradaic impedance; α the transfer coefficient; θ_a the phase angle between the resistive and capacitive components of the faradaic impedance; $n = 2$; and R, T, and F are as usual. At sufficiently high frequencies Imai and Delahay derived

$$\frac{1 + \mathrm{ctn}\,\theta_a}{1 + \mathrm{ctn}^2\,\theta_a} \approx \frac{1}{\mathrm{ctn}\,\theta_a} = \frac{i_a^o}{2^{1/2}\,nFCD^{1/2}}\,\frac{1}{\omega^{1/2}} \qquad (B)$$

where i_a^o is the apparent exchange density; C the bulk concentration of Hg(I); and $\omega = 2\pi f$, f being the frequency.

When the faradaic impedance Z_f is very large in comparison with the double layer impedance $1/\omega c_1$ (c_1 differential capacitance) one has $V_A \approx I_A/\omega c_1$ (I_A current amplitude) and there follows from the above equations:

$$\frac{\Delta\bar{E}_{\infty}\,\omega^2}{I_A^2} \approx \frac{1}{c_1^{\,2}}\,\frac{nF}{RT}\left[\frac{2\alpha - 1}{4} - \frac{\alpha i_a^o}{2^{3/2}\,nFCD^{1/2}}\,\frac{1}{\omega^{1/2}}\right] \qquad (C)$$

Imai and Delahay assumed that (a) the differential capacitance c_1 is not affected by variations of the Hg(I) concentration in the presence of a large excess of supporting electrolyte; (b) that c_1 is constant in the range of potentials corresponding to the variations in C; and (c) that c_1 is frequency independent. They stated that the first two assumptions were realistic and the third one verified experimentally. Further they assumed that i_a^o in this case is:

$$i_a^o = nFk_a^o C^{1-\alpha} \tag{D}$$

where k_a^o is the apparent rate constant. It then follows from Eqn. C that the ratio of the slopes of the plot $\Delta\bar{E}_\infty \omega^2/I_A^2$ against $\omega^{1/2}$ for two concentrations of Hg(I) C_1 and C_2 is $(C_2/C_1)^\alpha$. The coefficient α can then be evaluated from the directly measurable quantities $\Delta\bar{E}_\infty$, I_A, and ω without independent determination of the differential capacitance c_1. The latter was then evaluated from the intercept of the line $\Delta\bar{E}_\infty \omega^2/I_A^2$ against $\omega^{-1/2}$ for $\omega^{-1/2} = 0$. Finally i_a^o was calculated from the slope of the line $\Delta\bar{E}_\infty \omega^2/I_A^2$ against $\omega^{-1/2}$.

Rectification voltages were measured directly from a cathode ray oscilloscope display.

Because of the three assumptions stated above Imai and Delahay used a differential capacitance of 43 microfarads cm^{-2} in all calculations. The experiments were carried out at 24 ± 2° C in 0.1 and 0.2 <u>M</u> perchloric acid for concentrations of mercurous perchlorate from 5.8×10^{-5} to 4.7×10^{-4} <u>M</u> and in 1.1 <u>M</u> perchloric acid for 6.7×10^{-5}, 3.5×10^{-4}, and 7.3×10^{-4} <u>M</u> mercurous perchlorate. A transfer coefficient $\alpha = 0.28$ was determined and rate constants of 0.28, 0.36, and 1.3 cm sec^{-1} for 0.1, 0.2, and 1.1 <u>M</u> acid media, respectively.

To explain the large difference in rate constants found in 1.1 M perchloric acid by this technique from that found in 1.0 M perchloric acid by the double-pulse galvanostatic method the authors suggest that a coupled chemical reaction may be involved, that for the very high frequencies employed in their rectification study the effect of the chemical reaction is minimized or eliminated, while on the time scale of the galvanostatic experiments the effect is present and essentially constant. The authors did not determine what chemical reaction could be occurring.

Sluyters and coworkers, using the principles of complex-impedance plane analysis of faradaic impedance data, investigated the behavior of mercury electrodes in perchloric acid solutions. Sluyters-Rehbach and Sluyters (32) measured the differential capacitance at the dropping mercury electrode at 25^0 C for solutions containing mercurous perchlorate in 1 M perchloric acid from -0.305 to +0.717 volts versus the normal hydrogen electrode, and at frequencies from 420 to 5000 cps. The differential capacitance was shown to undergo a quite rapid increase for potentials anodic of +0.400 volt as had been shown by Grahme (11). The same authors then repeated this work with a hanging mercury drop electrode and with closer attention to the correction for electrolyte resistance (33). The resulting capacitances were somewhat lower than those previously determined, but the increase in capacitance with increasing anodic potential was still present. From the absence of charge-transfer polarization they concluded that for 1×10^{-3} $\underline{M}$ mercurous perchlorate in 1 $\underline{M}$ perchloric acid at 25^{0} C, the exchange current density must be in excess of 0.46 A cm^{-2}. The same conclusion was obtained for 1×10^{-3} $\underline{M}$ mercurous perchlorate in 0.1 $\underline{M}$ perchloric acid (33).

These authors also compared the results of this complex plane analysis with those of the double-pulse galvanostatic and faradaic rectification techniques (34). They attributed the lower exchange current density values from the double-pulse galvanostatic technique to a consistent systematic error in the galvanostatic data. Based on the absence of any indication from the faradaic impedance data at intermediate frequencies of the intervention of any process other than diffusion they discredited Imai and Delahay's attempt to explain this by a coupled chemical reaction.

From a numerical evaluation of the approximations made by Imai and Delahay in their faradaic rectification study Sluyters-Rehbach and Sluyters calculated that the error in measurement of exchange current density in the experiments of Imai and Delahay was within ten percent only if $\operatorname{ctn} \theta_a - 1$ is greater than four. Thus Eqn. B was only significantly justified with the results obtained for the highest Hg(I) concentration in 0.1 $\underline{M}$ perchloric acid. In all other cases the assumptions of Imai and Delahay were unjustified and their conclusions based on incorrect interpretation of their data, especially for the measurements in 1.1 $\underline{M}$ perchloric acid. Sluyters-Rehbach and Sluyters, on the assumption of pure control by diffusion of reactants, calculated values for the differential capacitance at equilibrium potentials corresponding to several Hg(I) concentrations from the data of Imai and Delahay and found reasonable agreement with the results of their own complex-plane analysis.

Birke and Roe (3) investigated the kinetics of the system Hg(I)/Hg to amplify an extension of the theory of the simple galvanostatic technique to permit rigorous application of a linearized η vs $t^{1/2}$ relationship for extrapolation beyond mass-transport control in studies of systems in which the reduced component is of unit activity. A preimpulse to abruptly charge the double layer was applied in order to assure a linear plot over an extended period on which to base the extrapolation to zero time.

The constant current was obtained from a 3 to 12 volt battery source. A mercury wetted contact relay applied a transient-free voltage step to the bridge (bridge circuit which balances out the resistance voltage drop of the cell). To control the charging spike it was necessary to shape the leading edge of the voltage step with a low pass filter.

The current step was applied to the cell at a fixed time during the growth of a mercury drop. The time cycle was derived from two microswitches activated by motor driven cams. One microswitch controlled a relay which dislodged the drop through a shearing force. The other switch, which was activated 4 seconds after the start of the growth of a new drop, triggered a wave form generator. The gate output of the generator activated the mercury wetted contact relay and the sawtooth output triggered the sweep of an oscilloscope. The duration of the sawtooth was about 6 msec and the sweep was initiated about 10 μsec before the relay contacts closed. The closing time of the relay was about 3 msec and was reproducible to about ± 10 μsec. A zero base line of one to three centimeters could thereby be observed on the oscilloscope screen.

The oscilloscope was equipped with a Tektronix Type D preamplifier. At maximum sensitivity the upper band pass limit of this unit was adequate to produce accurate measurements after two or three microseconds. The initial portion of the overpotential-time curve was somewhat attentuated and therefore unuseable.

These authors assumed the differential capacitance to be constant at 36 microfarads cm^{-2}. Kinetic data were taken for the anodic dissolution process in solutions 4×10^{-4}, 2×10^{-3}, and 4×10^{-3} M mercurous perchlorate at 24 ± 1^{0} C. Apparent exchange currents were determined at three current densities for each solution with satisfactory repeatability. A transfer coefficient of $\alpha = 0.25$ was determined. A $k_a^o = 0.06 \pm 0.02$ cm sec^{-1} can be determined from their data.

The most recent investigation of the kinetics of the system Hg(I)/Hg is that of Weir (36) using the current impulse technique (37). To supply the current impulse to the cell a General Radio 1217-B pulse generator with its associated power supply was used. The pulse generator was coupled to the cell through a 1-kiloohm load resistor to assure constant impulse current and two 1N-914 switching diodes with polarity appropriate to pass a pulse but to reject counterflow of current. With this input arrangement, current pulses continuously variable in amplitude from 0 to 20 ma and of duration as brief as 100 nsec were applied to the cell.

The overpotential response to the constant perturbation was amplified by a Tektronix 1121 amplifier (rise time 21 nsec). The amplified signal was cabled to a Tektronix 535A sweep-delay oscilloscope with a type H plug-in preamplifier (rise time 31 nsec).

With this system an over-all deflection sensitivity as great as 5 $\mu v\ cm^{-1}$ was achieved on a 100 nsec cm^{-1} time base. With appropriate calibration, current, overpotential, and time could be measured with an accuracy of 1%.

The system 10 - 90% rise time was less than 100 nsec; however, overshoot and transient ringing due to uncompensated inductance and stray capacitance prohibited reliable (±100 μv) observation of relaxation for an interval of up to 400 nsec following termination of the current pulse. Ringing was evident only following the pulse and did not obscure charging response.

Experiments were performed on seven concentrations from 2.05×10^{-5} to 5.15×10^{-3} M mercurous perchlorate in 1.00 M perchloric acid at 25^0 C. Estimates of differential capacitance were determined for each concentration by two different methods: (1) by direct calculation from the initial slope of the charging curve and the value of the constant charging current, and (2) by extrapolation of the relaxation data on a plot of log η against t to determine η_o and calculation of the capacitance from this value and the coulombic content (current x pulse duration) of the pulse. Estimates of differential capacitance obtained by the direct technique depended upon the current density at which the determination was carried out. The zero-current value of the capacitance was used as the appropriate differential capacitance at each concentration. A difference between the zero values found by the two different methods was observed which increased as the concentration increased. The differential capacitance was observed to increase with increasing anodic electrode potential, in striking agreement with the measurements of Sluyters-Rehbach and Sluyters. A reaction order plot showed excellent linearity in the low concentration region for both charging and relaxation data, but marked systematic departure from linearity was evident at higher concentrations for the points corresponding to the capacitance values determined in charging experiments. The slope of the reaction order plot established at low and intermediate concentrations is 0.68 ± 0.02. From the i_a^o values and α an apparent standard rate constant $k_a^o = 0.019 \pm 0.002$ cm sec^{-1} is calculated. This slightly higher result than obtained by the other transient methods was explained by the absence of partial mass transport control of the rate of the electrochemical reaction at short times.

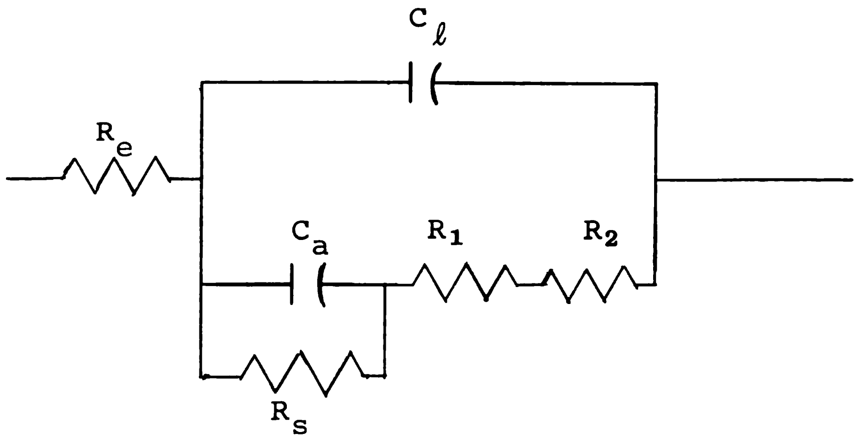
To resolve the anomolies of the dependence of differential capacitance calculated from charging curves upon current density and significant deviation from linearity in electrochemical reaction order plots for the higher concentrations, Weir developed a model (Figure 3) appropriate to the description of electrochemical processes involving adsorption of reactant and/or intermediate. Detailed analysis of the behavior of this network resolved the anomolous observations of his investigation and suggested the cause of the marked disparity between the kinetic results of the transient and the periodic relaxation techniques for this system.

Weir found no definitive mechanism could be determined directly from the predictions of this model and the experimental results. But through a re-evaluation of the data of Gerisher and Krause two unit charge-transfer steps were identified and rate control assigned to the first. Weir concluded that from this reaction sequence and the requirements of the model that the electrodeposition of mercury requires adsorption of reactant Hg_2^{2+} or intermediate Hg^{2+} prior to the charge transfer and postulated two alternate mechanisms:

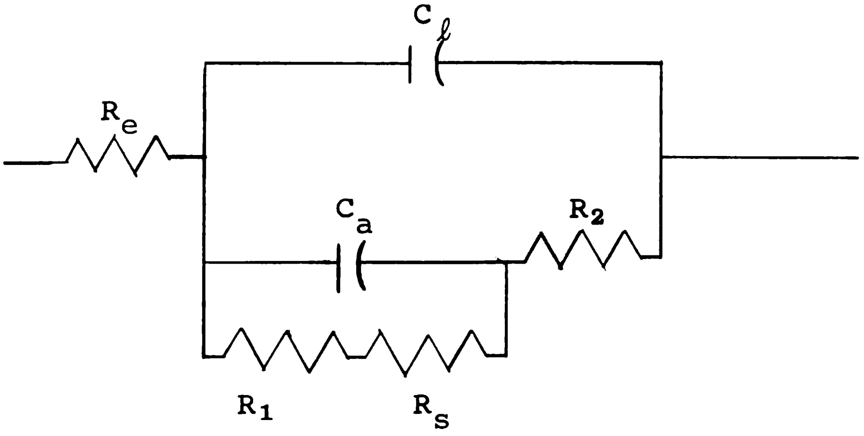
A) $Hg_2^{2+} + e^- \longrightarrow Hg_2^+$; $Hg_2^+ + e^- \longrightarrow 2Hg$

B) $Hg_2^{2+} + e^- \longrightarrow Hg_2^+$; $Hg_2^+ \longrightarrow Hg^+ + Hg$;

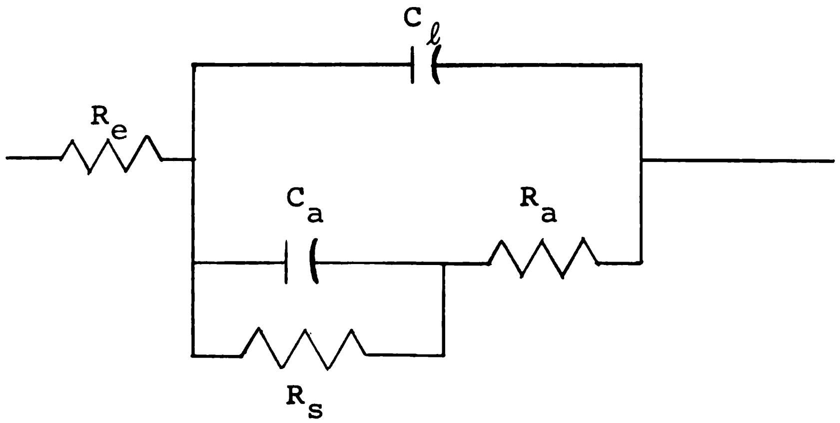
$Hg^+ + e^- \longrightarrow Hg$.



a) where discharge requires adsorption of reactant species.



b) where primary discharge of non-specifically adsorbed species precedes adsorption and discharge of intermediate.



c) general statement of both cases.

Figure 3. Circuit for Weir's adsorption model.

C_ℓ = electrochemical double-layer capacitance, R_e = electrolyte resistance, C_a = capacitance due to discharge of adsorbed species, R_a = charge-transfer resistance for discharge of adsorbed reactant or intermediate, R_s = adsorption resistance.

D. Summary of the Results of this Study Compared to Previous Studies

The current-impulse relaxation method used by Weir in his investigation was also used in the present investigation of the kinetics of the Hg(I)/Hg reaction. Constant current impulses of 0.2 μsec duration were applied to a hanging mercury drop electrode with a platinum gauze counter electrode in a solution of $Hg_2(ClO_4)_2$. The voltage-time relaxation curve was observed on an oscilloscope. A pulse of 1 μsec duration was used to obtain the charging curve. Concentrations of mercurous perchlorate from 5×10^{-6} to 1×10^{-2} in 1.0 <u>M</u> $HClO_4$ at 25° C were used.

Estimates of the differential capacitance were obtained by the same two methods used by Weir. And as observed by Weir the differential capacitance obtained by the direct method was dependent upon the current density at which the determination was carried out. The zero-current value of the capacitance was used as the appropriate differential capacitance at each concentration. Also as observed by Weir and Sluyters-Rehbach and Sluyters the differential capacitance increased with increasing anodic electrode potential. A reaction order plot showed excellent linearity in the intermediate and high concentration regions but departed from linearity at low concentrations. The slope of the reaction order plot established at intermediate and high concentrations is 0.67 ± 0.02. The i_a^o values were slightly higher than observed by Weir. This is explained by the fact that his relaxation data were obtained 0.6 μsec after the impulse whereas in the present investigation data were obtained starting at 0.2 μsec after the impulse hence a steeper slope was obtained. From the i_a^o values an apparent standard rate constant $k_a^o = 0.0297 \pm 0.002$ cm sec^{-1} was determined.

The kinetic results of the present investigation and of previous studies of the electrochemical reduction of Hg(I) are summarized in Table (1).

Table 1. Comparison of present kinetic results with the results of previous studies.

Investigations	Technique	Ref.	Approximate time before measurement	Apparent Transfer Coefficient	Std. rate Constant cm-sec^{-1}	Apparent Exchange Current Density $1\text{x}10^{-3}$ $\underline{M}$ $Hg_2(ClO_4^-)_2$ amp-cm^{-2}
Gerisher and Staubach	Faradaic Impedance	13	--	0.3 ± 0.2	0.0039	0.16
Gerisher and Staubach	Potentiostatic	13	10 μsec	0.4 ± 0.1	0.0015	0.07
Gerisher and Krause	Double-pulse galvanostatic	12	2-3 μsec	0.30 ± 0.03	0.0102	0.13
Matsuda, Oka, and Delahay	Double-pulse galvanostatic	20	2-3 μsec	0.30 ± 0.02	0.0194	0.25
Imai and Delahay	Faradaic rectification	16	--	0.28 ± 0.03	1.3	13
Sluyters-Rehbach and Sluyters	Faradaic impedance	33	--	nc*	nc*	$\geq$0.46
Birke and Roe	Modified galvanostatic	3	2-3 μsec	0.25 ± 0.05	0.06	0.38
Weir	Current-impulse	36	0.4 μsec	0.32 ± 0.02	0.019	0.30
Kudirka	Current-impulse	--	0.2 μsec	0.33 ± 0.02	0.0297	0.55

*"nc" -- Not calculated by authors.

II. EXPERIMENTAL

A. Reagents

The mercury used in this investigation was purified in this laboratory by repeated washings with 1 M nitric acid, 1 M NaOH, and distilled water, and filtering. The red mercuric oxide used in the preparation of solutions of mercurous perchlorate was Matheson, Coleman and Bell A.C.S. Reagent grade, perchloric acid was G. Frederick Smith double-distilled lead free acid at 70% strength. The distilled water used in the preparation of solutions and in cell rinsing was obtained by redistillation over $KMnO_4$ and NaOH in an all Pyrex apparatus, of laboratory distilled water. Nitrogen gas introduced into the cell was Liquid Carbonic prepurified gas, treated and passed into the cell by a glass and teflon purification train. The nitrogen was dried over calcium chloride, then passed through an oven containing copper turnings at 350^0 C to remove traces of oxygen, then through a multiple element trap containing activated coconut charcoal at liquid nitrogen temperature, and finally presaturated by bubbling through 1 M perchloric acid before introduction into the cell.

B. Solutions

Aqueous perchloric acid used as supporting electrolyte was prepared volumetrically to approximately 1 M concentration, then determined by titration with 2-amino-2-hydroxymethyl-1-3-propanediol, and was found to always be 1.00 ± 0.01 M and was used without further adjustment of concentration. A stock solution of mercurous perchlorate was obtained by preparation of a solution of mercuric oxide in 1.00 M perchloric acid and its reduction by mercury metal. The solution was assayed gravimetrically as the chloride (8), and its concentration, in agreement with calculation, was 0.0515 ± 0.0004 M. Working solutions were prepared by volumetric dilution of this stock solution with 1.00 M perchloric acid. All solutions were stored over mercury and in the dark.

C. Cell and Electrodes

A two electrode system similar to that used by Weir (35) was designed and constructed (Fig. 4). Simply a tube of copper connected through a pyrex support to a platinum gauze counter electrode concentrically surrounding the platinum wire which terminates in the drop contact. A second contact is provided near the drop contact but outside the copper tube. The pulse current is applied through this contact with the copper tube held at ground, and the response is observed between the platinum inner conductor and

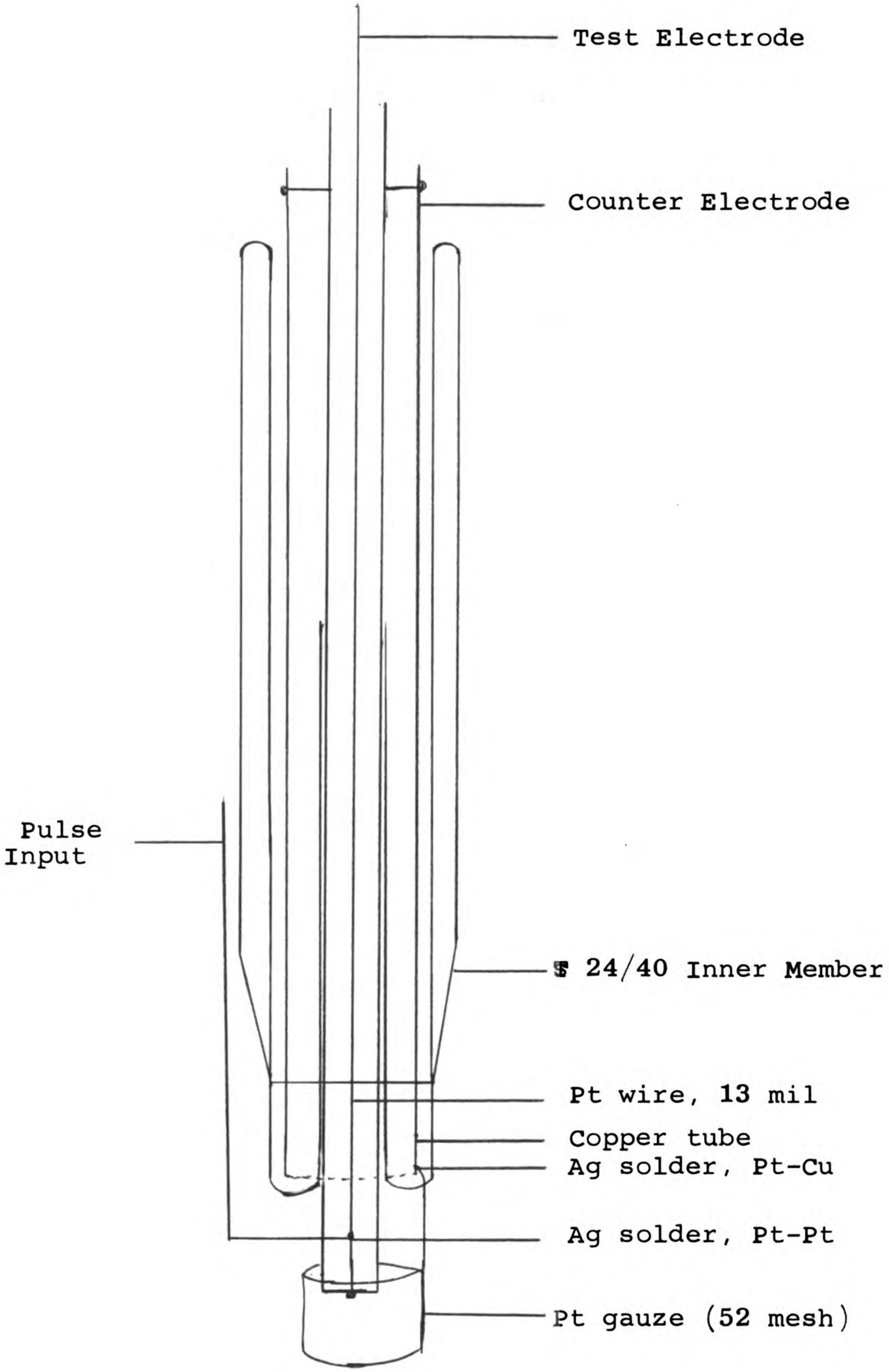


Figure 4. Electrode system for the present investigation.

the copper tube. The drop contact was polished flat and Hg plated according to Brubaker and Enke (4).

A Pyrex cell with standard taper ground glass fittings to accomodate this electrode, the dropping capillary, a teflon spoon, and a gas inlet was constructed.

The dropping capillary was a 6 - 12 sec drop time capillary from Sargent. It was fed from a 10 cc syringe as a reservoir, connected to a stand tube by a length of teflon tubing. The height of the mercury column was fixed at 610 ± 1 mm. Capillary data were established by measurement of period and mass for the discharge of 20 drops. The period was established using an electric stopclock (The American Time Co., Type S-1) and mass by weighing.

D. Instrumentation

The pulse generator used in this study was an Intercontinental Instruments Model PG-33. The maximum rise time/fall time is $\leq$6 ns depending on source impedance. The pulse duration of the generator is continuously variable from 30 ns to 1 sec, and frequency is variable from 0.1 cps to 10 mc and single shot. There are both positive and negative outputs from which current pulses adjustable from 10 ma to 200 ma can be obtained. This was connected to the electrode auxiliary contact by a tektronix 010-120 1X probe.

The detection system for the current-impulse experiments was composed of a Tektronix 556 sweep-delay oscilloscope with a Tektronix type 1A5 plug-in differential amplifier (8 nsec rise time). This was connected to the drop contact wire by a Tektronix 010-120 1X probe. Connectors of the BNC type were used for all terminations.

The pulse generator was triggered from the delayed-trigger output of the oscilloscope.

All current determinations for calculation of differential capacitance were made by connecting a 10.047 ohm resistor (its value determined by measurement with an ESI model 300 used as a Wheatstone bridge) between the pulse generator and the oscilloscope and measuring the voltage drop across it produced by a pulse of current.

Charging and relaxation curves were recorded photographically. A Tektronix type 350 camera with Kodak Tri-X1ASA 4001 35 mm film was used. The results from the negative strip were projected onto ruled graph paper and traced. All exposures were made with manual shutter control.

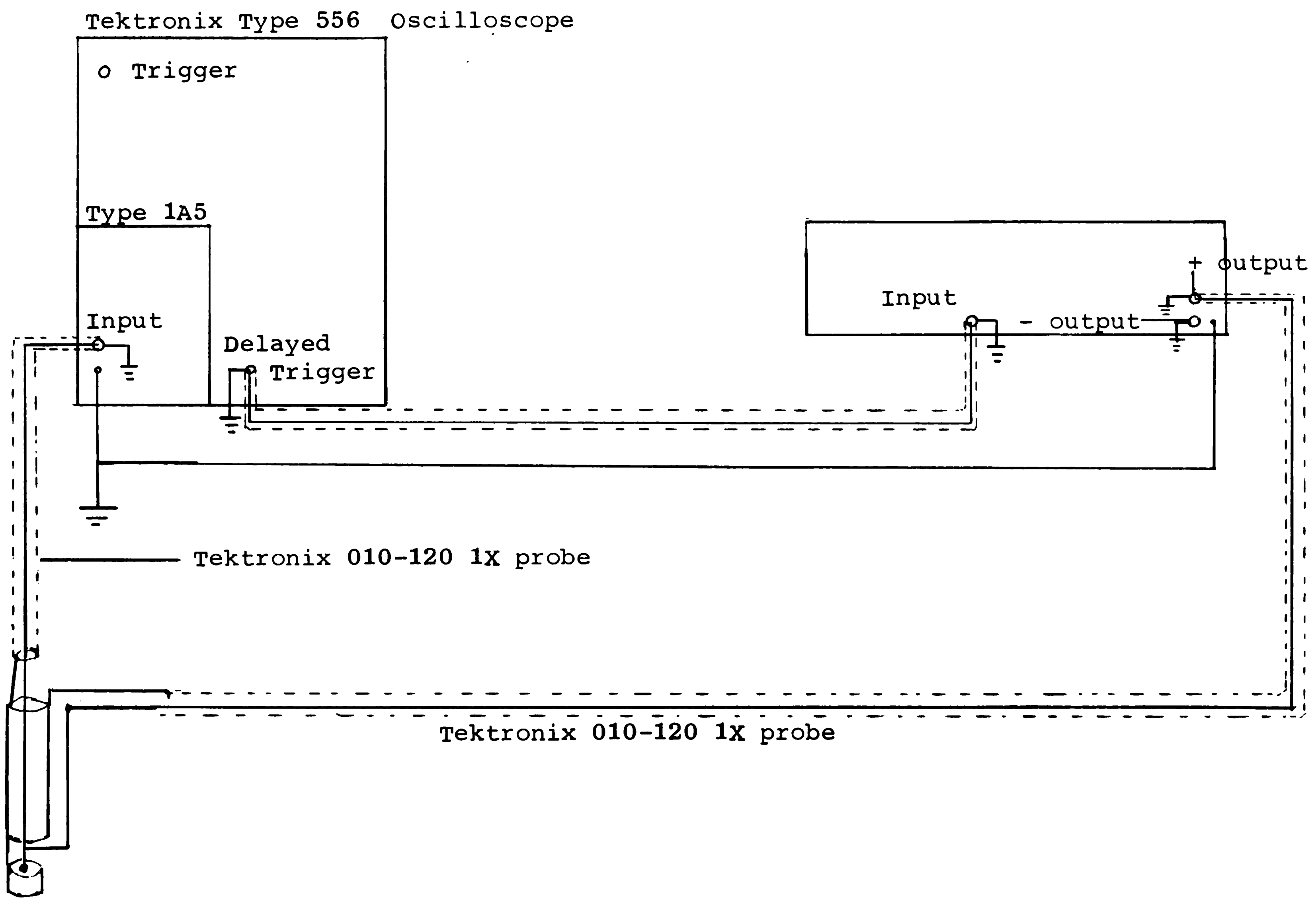


Figure 5. Schematic representation of interconnection of cell and instruments in the present investigation.

III. RESULTS

A. Capillary Data

Because the electrode potential of mercury in contact with an aqueous solution of a soluble mercurous salt is determined by the concentration of mercurous ion, it is necessary to make a separate determination of drop mass in each solution. The results of drop period (t*) and drop mass (m*) determinations for solutions from 5 x 10^{-6} to 1 x 10^{-2} M mercurous perchlorate in 1.00 M perchloric acid are summarized in Table (2).

Table 2. Drop period, drop mass, and spherical drop area in solutions of varying concentration of $Hg_2(ClO_4)_2$ in 1.0 M $HClO_4$.

Conc. $Hg_2(ClO_4)_2$ mole $liter^{-1}$	Drop Period (t*) sec $drop^{-1}$	Drop Mass (m*) mg $drop^{-1}$	Approximate drop area cm^2
5.12 x 10^{-6}	5.950	5.352	0.02650
1.024 x 10^{-5}	5.893	5.301	0.02590
2.048 x 10^{-5}	5.840	5.253	0.02570
5.12 x 10^{-5}	5.783	5.202	0.02555
1.024 x 10^{-4}	5.730	5.151	0.02540
2.048 x 10^{-4}	5.682	5.114	0.02525
5.12 x 10^{-4}	5.605	5.042	0.02504
1.024 x 10^{-3}	5.560	5.002	0.02490
2.048 x 10^{-3}	5.505	4.953	0.02474
5.12 x 10^{-3}	5.440	4.891	0.02454
1.024 x 10^{-2}	5.394	4.853	0.02440

Estimates of the drop area for each solution concentration were obtained by calculating the spherical area from each drop mass by the equation:

$$S = [36\pi(m^*/d_{Hg})^2]^{1/3}$$

taking the density of mercury at 25° C. The results of these calculations are also given in Table (2). These values were used for normalization of results to unit area.

B. Capacitance Data

Estimates of differential capacitance were obtained at each concentration by two methods: (1) by direct calculation from the initial slope of the charging curve obtained using a 1 μsec pulse and the value of the current and (2) by extrapolation of the relaxation data obtained using a 0.2 μsec pulse on a log $|\eta|$ versus t plot to $t = 0$ to determine η_o ; and calculation of the capacitance from this value and the coulombic content of the pulse.

As observed by Weir estimates of the differential capacitance obtained by the direct technique depended upon the current density at which the determination was carried out. The estimates obtained by the two methods were not at variance as observed by Weir until the two highest concentrations. Typical data for low, intermediate and high concentrations are given in Table (3) and illustrated in Figure (6). These data show strong dependence of differential capacitance from anodic charging current, increasing

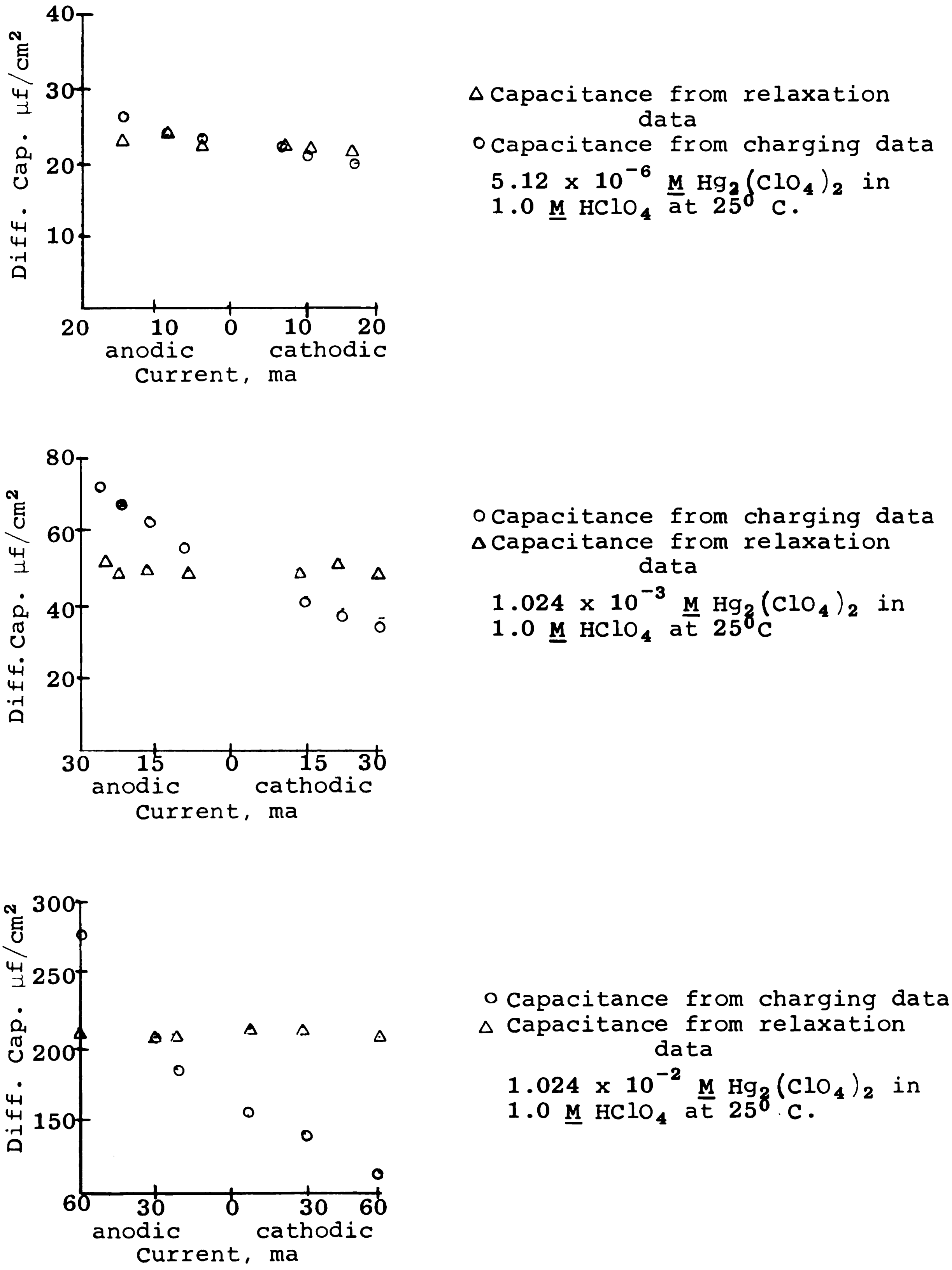


Figure 6. Differential capacitance from charging and relaxation procedures.

Table 3. Differential capacitance data from charging and from relaxation experiments for representative concentrations of $Hg_2(ClO_4)_2$.

Concentration mole/liter	Current, ma	Differential Cap. calc. from charging curves $\mu f/cm^2$	Differential Cap. calc. from relaxation plots $\mu f/cm^2$
5.12×10^{-6}	14 anodic	26.4	23.58
	9.2	23.14	23.94
	6.2	23.40	21.87
	6 cathodic	22.64	22.64
	9.8	21.13	23.48
	15	20.58	22.31
1.024×10^{-3}	29 anodic	72.5	51.5
	24	68	50.3
	17	62	52
	10	56	50.6
	15 cathodic	44	50
	23	40.5	51
	29	38.5	49.6
1.024×10^{-2}	60 anodic	270	210
	30	208	208
	20	190	206
	20 cathodic	150	210
	30	142	208
	60	118	208

with increasing anodic current, while for cathodic charging, the capacitance shows a distinct but decreasing trend with increasing cathodic current. The capacitance values obtained from the relaxation data do not show this trend but remain essentially constant for all currents. As demonstrated by Weir (36) the appropriate capacitance for either procedure is that corresponding to the zero current intercept of its current dependent values.

Thus zero-current estimates of the differential capacitance were obtained for all solutions by both procedures. These values are summarized in Table (4). These values are the average of four determinations.

Figure (7) shows the log differential capacitance plotted as a function of measured potential compared to the values of Sluyters-Rehbach and Sluyters obtained from their faradaic impedance study and to Weir's values of capacitance _vs_. equivalent potential calculated using $E^0 = 0.789$ (19). The agreement is very good until high potentials. The discrepancy here is most likely because of the shorter time at which the present data were obtained. With longer time more charge will be consumed by the faradaic reaction and thus Δq will increase and hence C_d increases. This will be more apparent at high concentrations.

Using a 2 μsec charge duration Weir stated he observed a steep initial curvature in the charging curves which was more prolonged the higher the concentration and more evident with lower than with higher cathodic current density. A

Table 4. Differential capacitance estimates for solutions of varying concentration of $Hg_2(ClO_4)_2$ in 1.0 M $HClO_4$.

Concentration mole/liter	Zero-current Cap. from relaxation plot μf/cm²	Zero-current Cap. from charging curve μf/cm²
5.12×10^{-6}	25.7	27
1.024×10^{-5}	28	27
2.048×10^{-5}	28.1	29.1
5.12×10^{-5}	28.8	29.0
1.024×10^{-4}	34.6	33.6
2.048×10^{-4}	33.8	35.4
5.12×10^{-4}	41.0	40.0
1.024×10^{-3}	50.0	52.2
2.048×10^{-3}	61.4	61.0
5.12×10^{-3}	118.4	102.5
1.024×10^{-2}	203	161.8

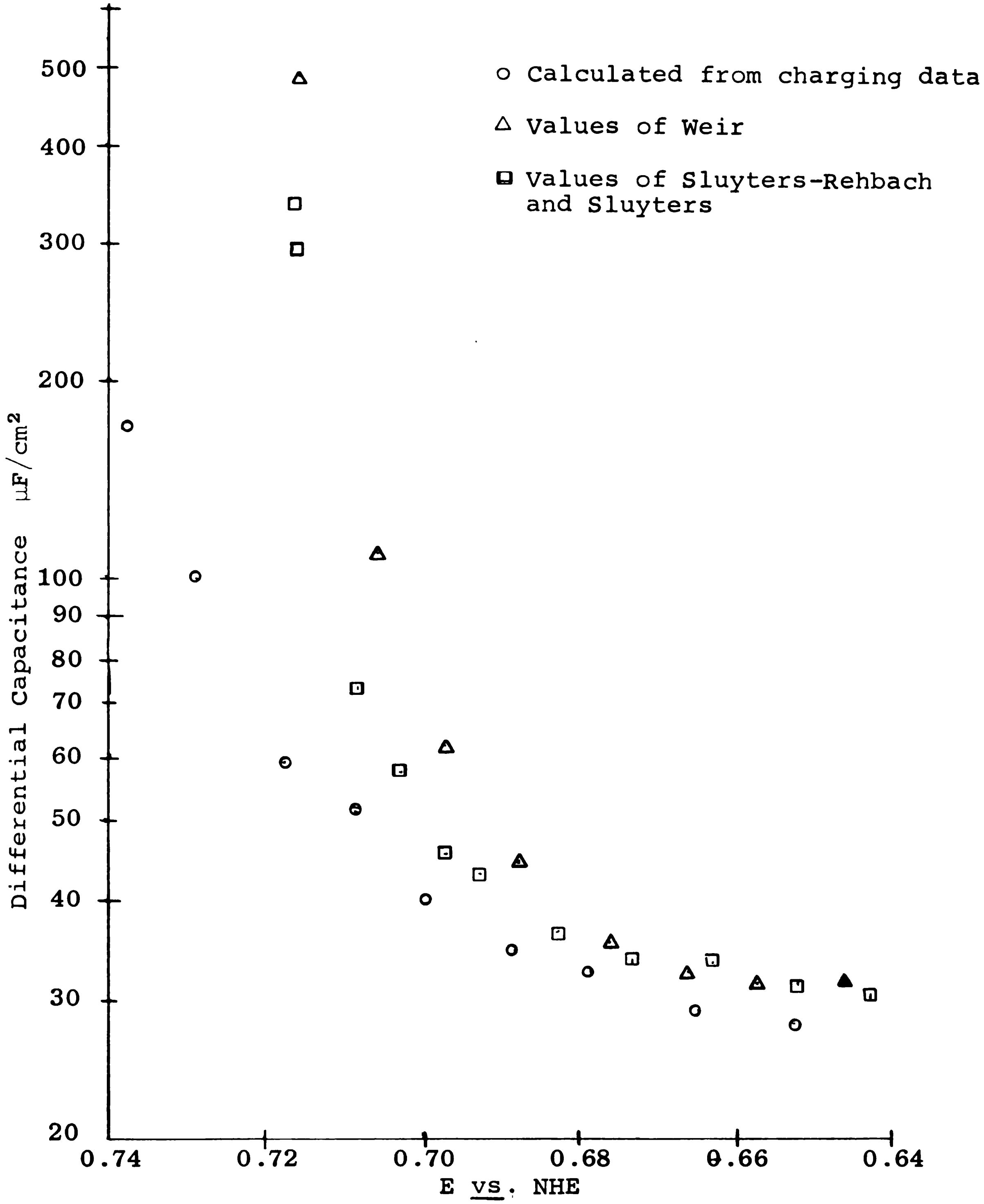


Figure 7. Differential capacitance as a function of potential.

1 μsec charge duration was used in the present investigation and the charging curves were observed to curve off. This was more marked at anodic currents and with higher concentrations and was attributed to the onset of the faradaic reaction. Typical charging curves are illustrated in Figure (8). The initial slope of these curves was used in all capacitance calculations.

Typical relaxation curves and semi-logarithmic decay plots with a pulse duration of 0.2 μsec are illustrated in Figure (9). Slopes of the log η versus t plots were taken from the initial portion of the curve. Since no portion of these curves is essentially linear something more than charge-transfer must be occurring.

Exchange current densities were determined for each concentration from graphically-estimated slopes of log η versus t plots prepared directly from the relaxation curves. The values of the apparent exchange current densities calculated from the two sets of capacitance values are summarized in Table (5).

A reaction order plot of these data is given in Figure (10). It shows excellent linearity with the exception of the low concentration region for both sets of data.

The slope of the reaction order plot is found to be 0.67 ± 0.02. On the basis of the simple reaction-order treatment given in the introduction, this corresponds to an apparent transfer coefficient of $\alpha = 0.33 \pm 0.02$. From the

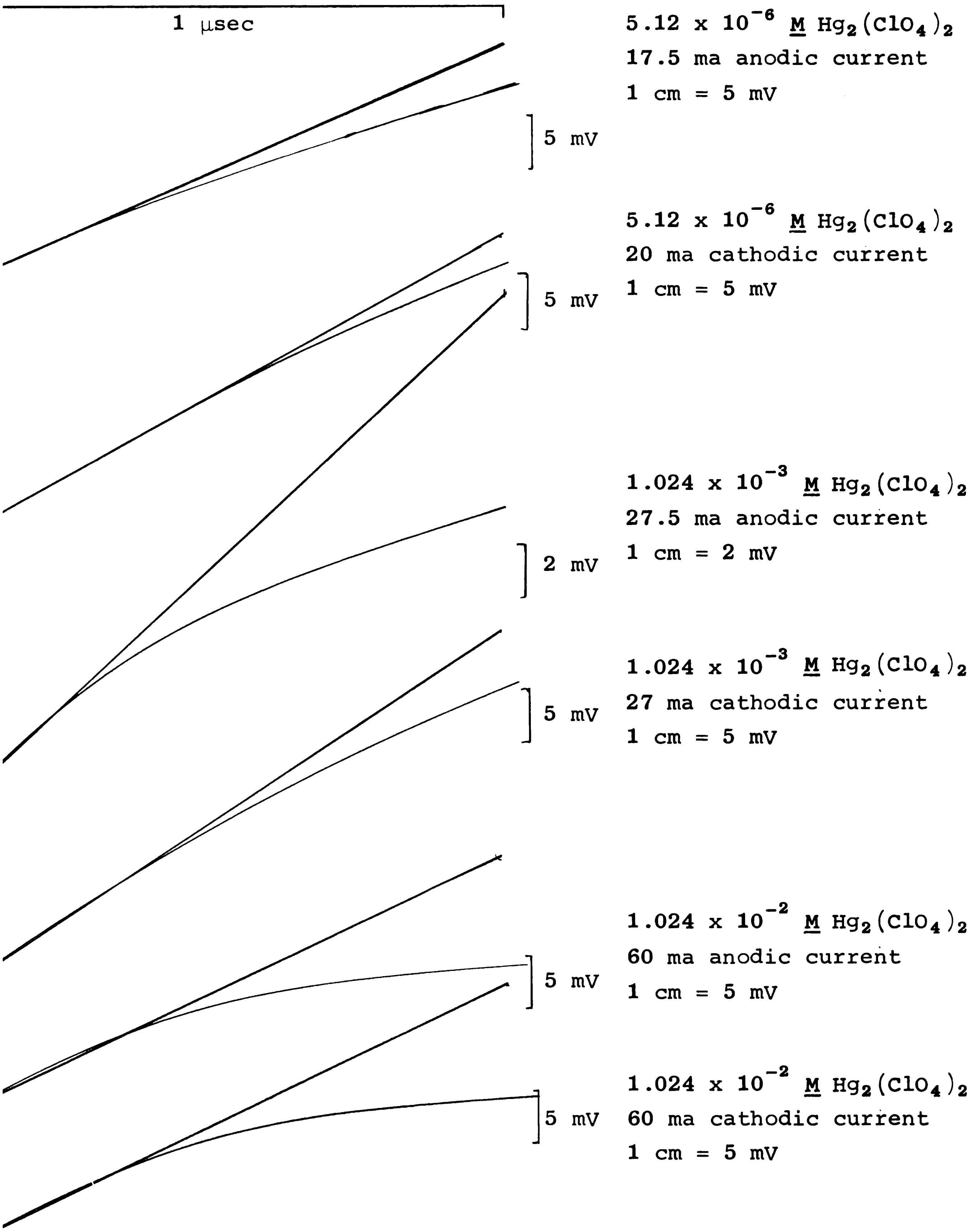
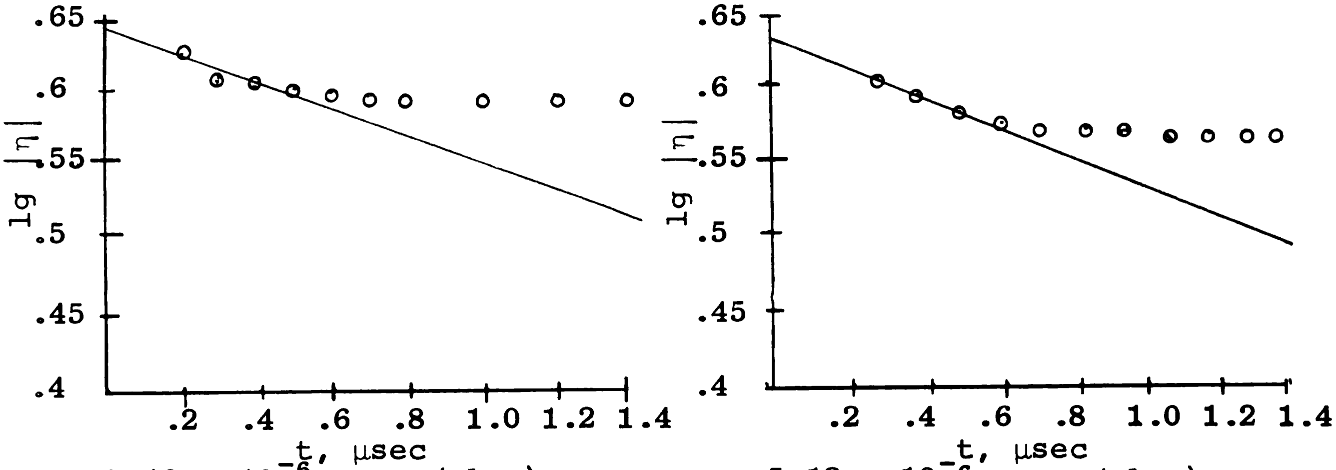
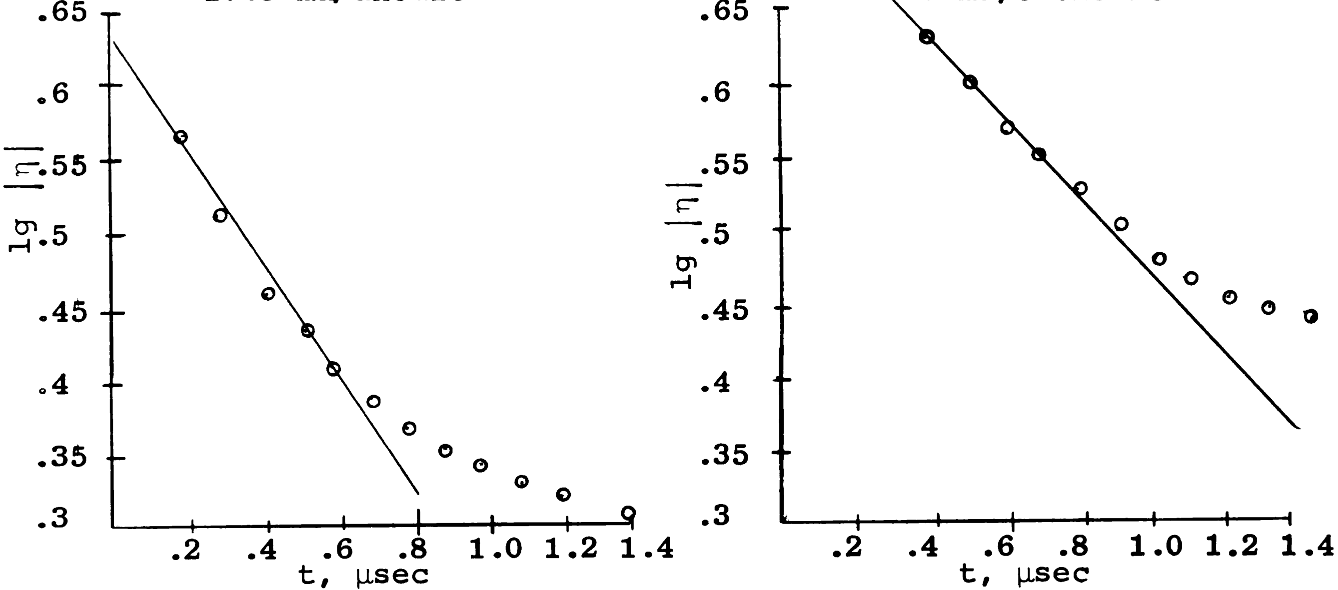


Figure 8. Typical charging curves.



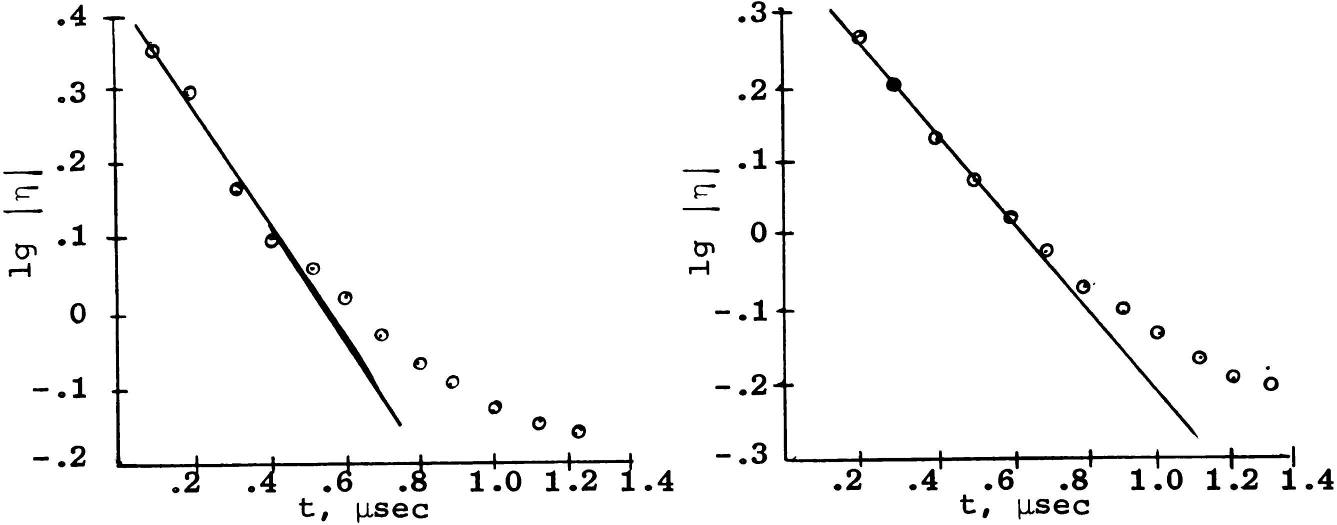
5.12 x 10^{-6} M $Hg_2(ClO_4)_2$
17.5 ma, anodic

5.12 x 10^{-6} M $Hg_2(ClO_4)_2$
15 ma, cathodic



1.024 x 10^{-3} M $Hg_2(ClO_4)_2$
29 ma, anodic

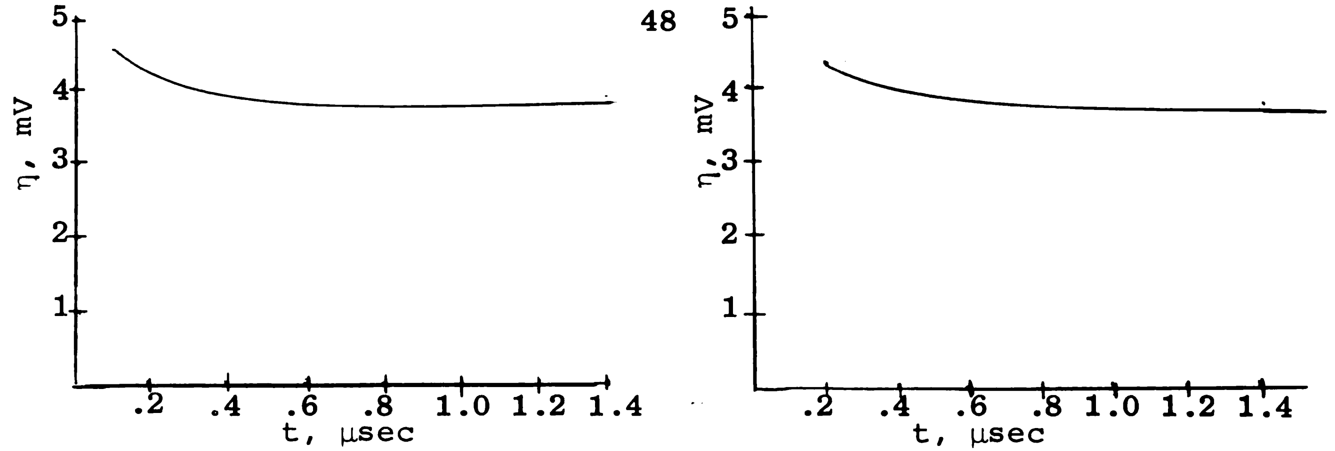
1.024 x 10^{-3} M $Hg_2(ClO_4)_2$
29 ma, cathodic



1.024 x 10^{-2} M ~~Hg~~$Hg_2(ClO_4)_2$
60 ma, anodic

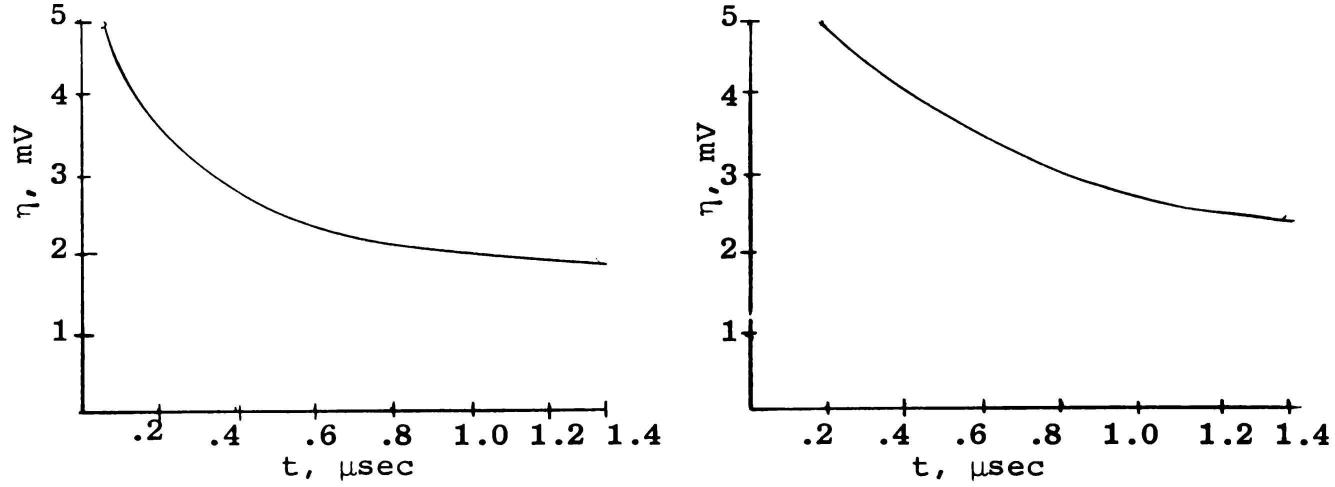
1.024 x 10^{-2} M $Hg_2(ClO_4)_2$
60 ma, cathodic

Figure 9. Typical relaxation and log η vs t curves.



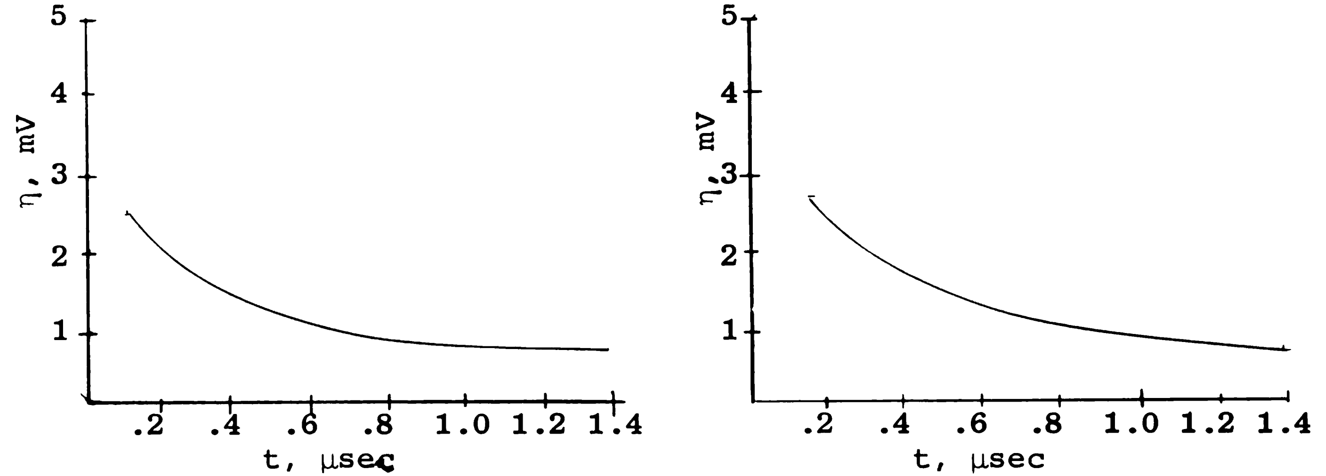
5.12×10^{-6} $\underline{M}$ $Hg_2(ClO_4)_2$
17.5 ma anodic

5.12×10^{-6} $\underline{M}$ $Hg_2(ClO_4)_2$
15 ma cathodic



1.024×10^{-3} $\underline{N}$ $Hg_2(ClO_4)_2$
29 ma anodic

1.024×10^{-3} $\underline{M}$ $Hg_2(ClO_4)_2$
29 ma cathodic



1.024×10^{-2} $\underline{M}$ $Hg_2(ClO_4)_2$
60 ma anodic

1.024×10^{-2} $\underline{M}$ $Hg_2(ClO_4)_2$
60 ma cathodic

Figure 9. (Cont.)

Table 5. Calculated apparent exchange current densities.

Concentration mole/liter	i_a^o from charging cap. amp/cm^2	i_a^o from relaxation cap. amp/cm^2
5.12×10^{-6}	0.0666	0.0636
1.024×10^{-5}	0.0763	0.0791
2.048×10^{-5}	0.0876	0.0871
5.12×10^{-5}	0.1040	0.0960
1.024×10^{-4}	0.1188	0.1233
2.048×10^{-4}	0.2102	0.2006
5.12×10^{-4}	0.3538	0.3564
1.024×10^{-3}	0.5561	0.5345
2.048×10^{-3}	1.0000	0.8994
5.12×10^{-3}	1.652	1.877
1.024×10^{-2}	3.281	4.235

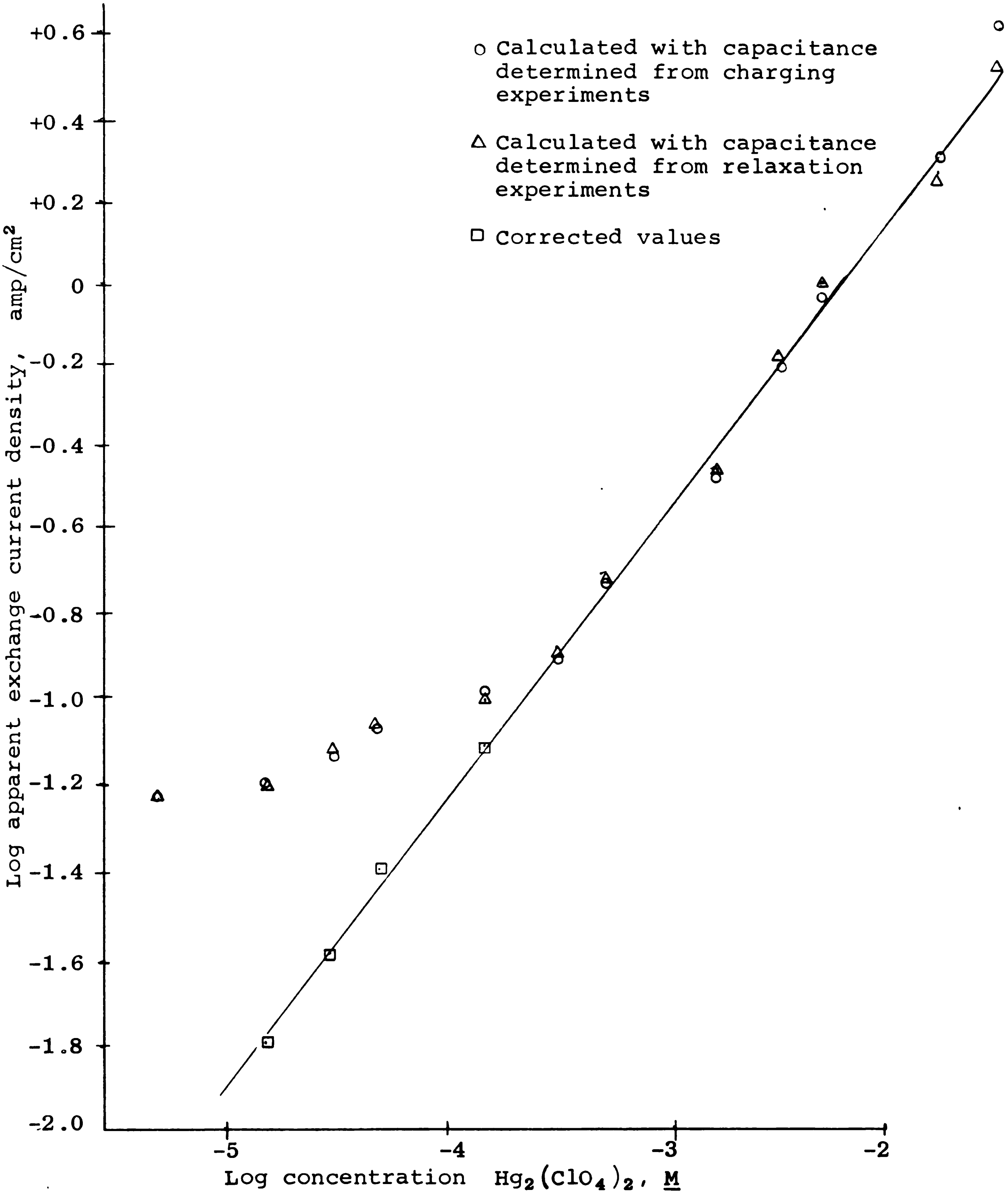


Figure 10. Reaction order plot in 1.0 M $HClO_4$ at 25° C.

i_a^o values and α, an apparent standard rate constant $k_a^o = 0.0297 \pm 0.002$ cm/sec is calculated

To explain the anomaly of the exchange current leveling off at low concentrations it was postulated that the mercurous monomer was contributing to the exchange current. A theoretical calculation of $i^o_{a\,total} = i^o_{a\,monomer} + i^o_{a\,dimer}$ did show a positive deviation from linearity at the low concentrations but did not correspond to the experimental curve for any value of k_d for the dimer $k_d = [Hg^+]^2/[Hg_2^{2+}]$.

It was then observed that a constant added to the theoretical exchange current for the dimer corresponded very well with the experimental data. Since the measured potential did not deviate from the linear Nernst slope at low concentrations it was concluded that the constant was not a contribution from the chemical system but must result from some other part of the experimental system.

On placing a resistance in parallel across the scope impedance it was observed that the initial slope of the log η vs t curve became steeper as the scope impedance decreased. Thus it was postulated that a system decay constant resulting from some reactance of the cell relaxing across the scope impedance is observed added to the decay of the electrode-solution interface.

By using 1×10^{-7} M mercurous perchlorate which has a much smaller exchange current than is equivalent to the system RC time constant, the system decay constant was measured.

From this $(RC)_{sys}$ a slope for this relaxation was calculated. By subtraction of this slope from the experimental curve, a curve assumed to correspond to solution-interface relaxation alone was obtained. The slope of the resulting curve was used to calculate a new exchange current value. This was done for 5×10^{-6} to 5×10^{-5} M $Hg_2(ClO_4)_2$ and the resulting exchange currents agree well with the theoretical exchange currents. These corrected values are given in Table (6) and plotted in Figure 10.

Table 6. Corrected values of apparent exchange current densities for low concentrations of $Hg_2(ClO_4)_2$

Concentration mole/liter	i_a^o from charging cap. amp/cm^2	i_a^o from relaxation cap. amp/cm^2
5.12×10^{-6}	0.0161	0.0159
1.024×10^{-5}	0.0249	0.0252
2.048×10^{-5}	0.0386	0.0380
5.12×10^{-5}	0.0795	0.0790

Comparison of the exchange current density result of 1.0×10^{-3} M mercurous perchlorate with that of previous studies shows that it is considerably higher than that found by any of the other methods except the faradaic rectification study of Imai and Delahay which has previously been disproved. It does agree with Sluyters-Rehbach and Sluyters' determination that it should be ≥ 0.46 amp/cm^2. The low results of the previous investigations can be explained by lack of correction for mass-transport. Weir's low results from the current-impulse data can be explained by the fact that data were not obtained until 0.6 μsec after the impulse.

CONCLUSION

Although the mechanism of reduction of mercury (I) cannot be established from the results of the present investigation, it has presented new data from which further investigation can proceed. Significantly, results have been obtained at much shorter times than previously and also the deviation of the exchange current from linearity at high concentrations as observed by Weir has been disproven.

By design of a more compact cell and use of a differential probe from the cell to the scope it is hoped that more significant data can be obtained on further investigation to explain why the differential capacitance increases with potentials anodic of +0.400 and to obtain a mechanism for the reduction of mercury (I).

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